THE PREPARATION AND PROPERTIES OF YTTRIUM MIXED METAL

BY

JOHN FREDERICK GROSS HICKS

B.S. University of Pennsylvania, 1906
M.S. University of Illinois, 1916

THESIS

Submitted in Partial Fulfillment of the Requirements for the Degree of

DOCTOR OF PHILOSOPHY

IN CHEMISTRY

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THE PREPARATION AND PROPERTIES OF YTTRIUM MIXED METAL.

I. Object of and Reasons for the Investigation.

On account of the meagreness of the work done,[1] because the metal has never been obtained in other than powder form, and because of the possibility of commercial application of the metal or its alloys, the preparation of coherent "Yttrium Mixed Metal"[2] (analogous to the well-known "Cerium Mixed Metal") was undertaken. It was further intended to make a detailed study of the properties of the metal and of its alloys with the common metals. Depending on the source of material, such a metallic product should vary in composition and "atomic weight."

II. Preparation of Materials.

Powdered gadolinite was decomposed by boiling conc. hydrochloric acid, and the mixed cerium and yttrium earths precipitated from the filtered solution by excess of oxalic acid. The "atomic weight" of these mixed earths (by oxide-oxalate ratio[3]) was 104.14. The cerium earths were almost completely removed as difficultly soluble double sulfates with sodium, $R_2(SO_4)_3.Na_2SO_4.8H_2O$, yielding mixed yttrium earths of "atomic weight" = 100.16. It should be noted that the term "atomic weight" here signifies an indication of relative purity of material for starting, or of product, on a basis of Y = 89; the numerical values are used in analytical calculations of metal content of product, the components of the mixture not being separable by ordinary analytical methods.

The soluble yttrium-earth sodium sulfates were converted to chlorides, and the crystallized chlorides mixed with an equal weight of ammonium chloride and partly dehydrated at 115°. Five of the 6 molecules of water of hydration were thus removed; the removal of the sixth causes hydrolysis.[4] Complete dehydration was effected in an atmosphere of dry hydrochloric acid gas at 350–400°. The product was a pinkish yellow

[1] Other investigators mention isolation of yttrium (pure metal), but only as incidental to other studies. Their accounts are, in the main, conflicting. See the following: Wohler, *Pogg. Ann.*, **13**, 577 (1828); Popp, *Inaug. Diss.*, Göttingen; *Ann.*, **131**, 186 (1864); Humpidge and Burney, *J. Chem. Soc.* (London), **35**, 115 (1879); Winkler, *Ber.*, **23**, 787 (1890).

[2] The name "Yttro-mischmetall" was originally proposed, but at the instance of Dr. C. W. Balke, it was changed to the present one, for the sake of analogy. Dr. Balke further pointed out that the term "Cerium Mixed Metal" officially means the alloy of cerium with the other cerium earth metals, as distinguished from pure cerium, and that the older term "Mischmetall" had been used to mean both, thereby resulting in confusion.

[3] *Z. anorg. Chem.*, **47**, 464 (1905); *J. Am. Chem. Soc.*, **38**, 2338 (1916).

[4] Oral communication by B. S. Hopkins.

powder, melting at 850–900° to a clear amber-colored liquid, which solidified to a gray mass.

C. Matignon[1] makes note of the difficulty of preparation of anhydrous yttrium chloride free from basic salt, but says nothing of the dehydration in hydrochloric acid gas. This modification of his method has been repeatedly used with success by workers in this laboratory on a small scale for atomic-weight determinations; although difficult, it can be worked successfully for large amounts. While the writer's results are in harmony with Matignon's as to the contamination of normal chloride by basic salt, they are in opposition to his finding that "Yttrium chloride is not appreciably volatile at temperatures slightly above its melting point;" in fact, serious loss resulted from this cause during some of the electrolyses. Hopkins and Balke[2] state, in connection with the purification of yttrium chloride, that its volatility "was a matter of some concern."

Rare earth material was recovered from wastes precisely as has been described for working up gadolinite, with the exception of the separation of the cerium earths from the yttrium earths.

III. Description of Apparatus.

The final form of electrolytic cell is shown in the diagram. The cathode was made by cutting a 7-inch piece from a 6-inch cylindrical graphite electrode, and boring it to a depth of 6 inches, the inside diameter being 4 inches. In service it was lined with a thick paste of "alundum cement," which covered the inner walls completely, leaving the bottom of the cell available as cathode. This decreasing of carbon surface reduced very materially the formation of metallic carbides. The refractory lining was not attacked by the bath. Radiation was reduced by packing "Sil-o-cel" or sand tightly around the crucible. The anode was a graphite rod, two inches square and about two feet long, suspended and adjusted as shown. Such a device is very unlikely to fail in service, and has the additional advantage of capability of adapting new electrodes without waiting for the

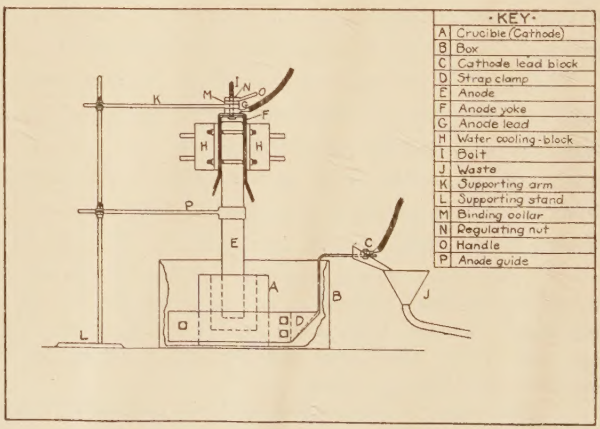

Fig. 1.—Electrolytic cell.

[1] *Compt. rend.*, **134**, 308 (1902).

[2] *J. Am. Chem. Soc.*, **38**, 2338 (1916).

furnace to cool. In case of the necessity for auxiliary heating, a common Fletcher 5-inch "solid flame" burner placed beneath the cathode box answered well.

The apparatus for the final dehydration of the earth chlorides consisted of a tube of hard glass or quartz, in which the partly dehydrated chlorides were placed, connected at one end with a hydrochloric acid generator and at the other with a fume absorber. This latter was a glass tube provided with water inlets, and it efficiently prevented both hydrochloric acid gas and ammonium chloride vapors from escaping into the air.

IV. Experimental Part.

The decomposition of the anhydrous chlorides by metallic sodium was first attempted by slowly heating a mixture of the two in small crucibles lined with a paste of "alundum cement" and magnesia. The results were very unsatisfactory, owing to incomplete reaction; passing sodium vapors through fused anhydrous chlorides was even less so. The product of some of the best runs by the former method was a powder somewhat resembling zinc dust in appearance, which the lens showed to be made up of a dark gray powder mixed with white particles. The entire mass was readily soluble in acids, and the usual "atomic-weight" determinations were therefore valueless, referring to total earth metal rather than to that liberated by the reaction. These methods were abandoned.

When the decomposition was carried out *in vacuo*, the reaction mixture was placed in iron or nickel boats, and these into seamless steel tubes. After exhausting to 3–1 mm., the charged tubes were inserted in a muffle previously heated to 1100°; the reaction took place quickly and quietly. This method was adopted as the best chemical means for decomposing the chlorides because: (1) oxidation was reduced to a minimum; (2) by-products efficiently removed; (3) ease and rapidity of manipulation. Admixed material was removed by shaking with anhydrous bromoform in a Harada separatory funnel, using anhydrous chloroform as a regulative diluent. This applies also to metal produced by electrolytic methods.

The resulting metal was a black powder, of "atomic weight" = 122.4 (original material = 104.3), and showed upon analysis:

	Per cent.
Metal (R = 122.4)	95.70
Iron	1.66
Undecomposed RCl_3	2.30
Oxygen (by difference)	0.34

The results indicate a simple and easy method for preparing such a "mixed metal" on a large scale and of relatively high purity.

In the electrolytic methods, the anhydrous chlorides (300–500 g.) were charged into the crucible cathode, and the temperature slowly raised to complete fusion, after which the electrolysis was carried out in the usual

manner. During both fusion and electrolysis a stream of dry hydrochloric acid was allowed to enter the crucible; this prevented hydrolysis by atmospheric moisture. The basic chlorides produced by such hydrolysis dissolve but slightly in the fused normal chlorides, as is shown by the formation of solid particles at the surface of the fused mass. These soon afterward sink, and it takes but a small quantity to render a bath viscous and unfit for further electrolysis. The addition of small quantities of common salt causes these particles to dissolve, and the bath reliquefies, but no good results were ever obtained after the pasty stage had once been observed. The corresponding phenomenon for cerium chloride seems not to have this ill effect.[1,2]

"Metal fog" was very noticeable in all electrolyses. The addition of salt, fluorspar, or calcium chloride had no remedial effect.

The "anode effect" was of quite frequent occurrence during the earlier experiments; runs in which it occurred were always worthless. Sometimes the evolution of halogen would recommence after interruption, but it was always thereafter intermittent.

Formation of carbides was also frequently noticed, until the matter of lining the crucible (except at the bottom) was worked out. In the case of baths of pure fused chloride, the carbide could only have been that of an earth metal; in the case where sodium or calcium salts had been added it could have been carbides of these metals. Indeed, it was always more noticeable in baths known to contain sodium, except the cryolite bath. The formation of carbides could be detected by the pungent "hydrocarbon" odor,[3] which was very noticeable as the bath cooled down; it is thought this is due to hydrolysis of carbides by atmospheric moisture. The absence of the odor during a run or when the bath was very hot, and the presence of it when the bath had been cooling for some time, might prove that the carbides decompose at a temperature below the melting point of the bath, and that they are formed as it cools, although it could with equal propriety be concluded that they are formed at the higher temperature but not hydrolyzed until the temperature becomes low enough to permit of the action of atmospheric moisture.

A series of small scale experiments was made with the object of determining which carbon electrode caused the formation of carbides. It was found that with carbon anode and iron or nickel cathode no "carbide odor" was noticed; with an anode not carbon and either metallic cathode, carbide odor was frequently noticed. This shows that a carbon anode is at least partly responsible for the formation of carbides during the course of an electrolysis.

[1] Hirsch, *Proc. Am. Electrochem. Soc.*, **20**, 57 (1911).

[2] Thompson, *Met. Chem. Eng.*, **17**, 213 (1918).

[3] A strong odor similar to that given off when commercial calcium carbide is hydrolyzed. It will hereafter be termed "carbide odor" for the sake of brevity.

Electrolyses were carried out using a current density of 6 to 10 amperes per sq. cm. at 10 to 13 volts; the temperature varied from 900° to 1100°, the best runs being made at about 1000°. The yield of such runs was a black powder, exactly like that produced by the chemical method above described; the average "atomic weight" was 120, and analysis showed:

	Per cent.
Metal (R = 120)	94.05
Iron	1.19
RCl (undecomposed)	0.82
Oxygen (by difference)	3.94

It is thus obvious that electrolytic methods will produce a material of the sort under discussion of equal purity with chemical methods, and perhaps of lower content of undecomposed material. The disadvantage of a higher percentage of oxide (doubtless due to the high temperature and much slower cooling) is apparent; this oxide may prevent coalescence when attempts at fusion are made. Loss by volatilization of yttrium chloride at this temperature (the crucible is open) has also been referred to as a disadvantage. It was estimated that about 1700 g. of chloride was lost by volatilization; the loss by recovery processes is very slight—less than one per cent. Some of the volatile material was condensed on a piece of glazed asbestos held over the crucible during a run; it was a yellow powder, reacting positively for rare earths, and faintly positive for iron. An "atomic-weight" determination yielded the value 52.7 for the earth present.

Another series of electrolyses was made using a solution of 50 g. of yttrium earth oxides (atomic weight of metal present = 104.6) and 250 g. of cryolite. The charge was fused and electrolyzed in the usual way. Blank runs showed that with cryolite alone no aluminium was deposited. The cryolite dissolved the oxides completely although slowly, but the solution is not so good a conductor as well-made fused chlorides; the bath is much easier to prepare, however. During the electrolysis carbon monoxide was slowly evolved, and a great deal of "metal fog" was produced. More difficulty in separating metal and flux was also experienced. Runs were made using a current density of 55–65 amperes per sq. cm. at 12–13 volts; the temperature ranged from 1200° to 1300°. The metal produced was lighter in color than that produced by the other electrolyses, showed an "atomic weight" = 118.5 and contained 0.68% iron.

V. Properties of "Yttrium Mixed Metal."

Considering the fact that no attempt was made to separate yttrium (Yt = 89) from the other earths (R = 152–174) associated with it, the average "atomic weight" of the metal produced (120) by the methods given is in no way different from what was expected. Other similar products prepared in future from "yttrium material" will just as certainly

yield different "atomic weights" on account of the wide limits between which the composition of rare earth minerals varies. If, for the sake of convenience, we assume the atomic weight of yttrium = 90 and that of the non-yttrium portion = 150 (instead of 152, the lowest atomic weight of the associated earths) it is apparent that the value 120 for the "atomic weight" of the metallic product signifies a yttrium content of 50 atomic per cent.; the percentage of yttrium by weight will then be 37.5.

The metal, separated as completely as possible from foreign material, was placed in a crucible of fused magnesia and sintered together in a vacuum furnace of the Arsem type, under a vacuum of one mm. or less. Accurate temperatures were not obtained; a pyrometer would not give trustworthy results with the furnace employed, owing to the constant variation in the intensity of the light within the furnace and a series of intermittent flashes across the carbon helix used as a heating element. This furnace will maintain a state of fusion with 600 g. of pure iron for an indefinite period when operating under a power of 10,800 watts; a power of 12,000–14,000 watts operating for nearly an hour only resulted in a sintering together of a 200 g. charge of yttrium mixed metal. While these results may be indicative of a high melting point, it must be remembered that the small amounts of oxide present could prevent coalescence in a relatively low-melting metal, as is true of aluminium and zinc.

The sintered metal was bluish gray in color, not of very high luster, although capable of taking a good polish; contact with air soon tarnished it. The sample examined contained 0.32% carbon and had $d_{15}^{15} = 5.508$. It burns at a rather low temperature in the air, with a bright flash like magnesium, leaving a residue of light brown oxide. It is slowly oxidized by moist air at room temperatures. The powdered metal glows when heated in an atmosphere of hydrogen, nitrogen or carbon dioxide; the products of the first two reactions are pale yellow in color and the nitride(?) is readily hydrolyzed. The glowing in carbon dioxide is accompanied by the evolution of carbon monoxide. Neither powdered nor sintered metal shows any tendency to amalgamate with mercury. Both yield the characteristic "carbide odor" (see *ante*) although an odor somewhat suggestive of phosphine was noticed at times. As the metal decomposed water at room temperatures and contained carbon, hydrolysis of carbides contained in it is very likely the cause of the odor. The metal decomposes warm or hot water quite rapidly, and dilute acids react violently with it. A solution of 0.2 cc. glacial acetic acid in 25 cc. of 95% alcohol will "etch" the sintered material sufficiently for metallographic purposes in 10 seconds.

The sintered metal fell to pieces in time (even disintegrating to a powder) especially if exposed to the air. Grinding and rough polishing seemed to accelerate disintegration, most of the specimens behaving in

this manner in course of preparation. Only two were obtained which could be studied, and these were highly unsatisfactory. Owing to the small size of specimens and the ease with which they disintegrated, hardness tests were deferred. The metal is with difficulty scratched with a file, although small pieces are pulled out by a file; it is pyrophoric, although not highly so in the sense of the modern "pyrophoric alloy."

Owing to the difficulties encountered in polishing (chipping out of small pieces, "dragging," scratching and tarnishing) satisfactory photomicrographs were not obtained. The rapid tarnishing prevents good definition. In general, the field was divided into two portions, one of which is dark and has somewhat the characteristic "eutectic structure" under the microscope. The other and lighter portion shows a complex structure of interlocked crystals, although not sharply defined. Unetched specimens did not yield photomicrographs owing to the ease with which the surface of the metal "dragged" under polishing. The darker component is the softer, the lighter crystalline material showing in relief after polishing.

VI. Summary.

1. This research was merely a preliminary study of the conditions necessary to produce "yttrium mixed metal" analogous to "cerium mixed metal."

2. The method of preparing anhydrous chlorides of the yttrium earth metals has been extended from the scale of atomic-weight determinations to that of large scale operations.

3. Yttrium mixed metal has been prepared in powder form by decomposing the anhydrous chlorides with sodium *in vacuo* and by the electrolysis of these chlorides in the fused condition.

4. Electrolysis of a solution of the oxides of the yttrium earth metals in fused cryolite has been studied; it is a less efficient method than the previous ones.

5. Loss of yttrium chloride by volatilization has been demonstrated.

6. Yttrium mixed metal has been obtained in coherent form for the first time by sintering the metal powder *in vacuo*. The resulting mass tends to disintegrate while metallographic specimens are being prepared from it, and upon exposure to the air.

7. Some of the properties of "yttrium mixed metal" have been recorded.

8. Further work in the preparation of the metal and its alloys is contemplated.

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VITA.

The writer was born in Philadelphia, August 31, 1884. He received his early training in the lower schools of Philadelphia, later in the Central High School of that city and entered the University of Pennsylvania, receiving therefrom the degree of Bachelor of Science in Chemistry, 1906. Since that time he has held the following positions:

Instructor and demonstrator in Chemistry, Medico-Chirurgical College of Philadelphia, 1906–1907.

Instructor in Chemistry, Villanova College, 1907–1908. Second semester, 1907, held this and the above position.

Associate Professor in Chemistry, Villanova College, 1908–1909.

Professor of Chemistry, Villanova College, 1909–1910.

Assistant Chemist in charge of Naphthalene Division, Barrett Manufacturing Company, 1910–1912.

Chief Chemist, Modoc Company, Inc., Fernwood, Pennsylvania (boiler compound, soap powders, sizes, horticultural chemicals), 1912–1914.

Associate Professor in Chemistry, Oklahoma Agricultural and Mechanical College, Stillwater, Okla., 1914–1915.

Assistant in Chemistry, University of Illinois, 1915–1918. (Master of Science in Chemistry, University of Illinois, 1916.)